Shaw The Shaw Group Inc.

Sequential Biological Destruction of Mixed Recalcitrant Groundwater Contaminants

Presentation Overview

- Project Background and Site Description
- Overview of Bench-scale Test
  - Methods, results and conclusions
- Overview of Pilot-scale Test
  - Anaerobic Reactor
    - Methods, results and conclusions
  - Aerobic Reactor
    - Methods, results and conclusions
- Summary of Pilot Test Results
- Conclusions
- Next Steps

Site Vicinity: San Diego County, Coronado, CA.

Project Background

- Former chemical waste disposal area (CWDA)
  - Late 1940s through mid 1970s
  - Disposed of every liquid chemical waste generated
  - Reported up to 32,000,000 gallons
- March 1997: Navy installed interim 3,000 scfm SVE system for soil
- September 1998: Identified large volume of LNAPL underlying the site
- September 1999: Initiated pilot-scale steam injection to enhance SVE
- May 2002: Phase II full-scale steam-enhanced SVE and product removal system
  - Generated groundwater that required treatment and disposal
  - Navy focused on innovative, destructive technologies

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Groundwater Treatment Bench Test

Groundwater Treatment Bench Test

- **Objectives**
  - **Determine if *ex situ* biological processes viable for treatment of Site 9 groundwater**
    - **Evaluate using anaerobic and aerobic reactors**
    - **TCE primary target contaminant for anaerobic**
    - **COD primary target for aerobic**
  - **Determine optimum sequence of biological processes and shortest possible hydraulic residence time (HRT)**
- **Navy interested because if effective, this approach could provide a cost-effective solution for other complex DOD groundwater problems**

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First Anaerobic Reactor Test: SBR

- Bench-scale 1-L static bed reactor (SBR) constructed of PVC
  - Seeded with primary anaerobic sludge from a pulp and paper plant
  - Filled with plastic media to a settled bed height of 6 inches
- Operating conditions
  - HRT – 13 hours
  - Temperature - 99°F (37°C)
  - Nutrient (28 mg/L NH_4Cl and 11.7 mg/L K_2HPO_4)
- Results indicated greater than 70% TCE/TCA reduction at a 13-hour HRT
- Economic considerations (full-scale); needed to reduce HRT in reactor to 5 hours or less

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Second Anaerobic Reactor Test: FBR

- **Modified 1-L SBR to a fluidized bed reactor (FBR)**
  - Seeded with primary anaerobic sludge from a pulp and paper plant
  - Filled with granular activated carbon (GAC) to a settled of 6 inches
    - Larger surface area
    - Simultaneous adsorption and degradation processes
  - Initially fluidized to 9.6 inches (60% fluidization)
- **Operating conditions**
  - HRT – 4 hours
  - Temperature - 99°F (37°C)
  - Electron donor (methanol), Nutrient (450 mg/L of NH_4Cl and 95 mg/L of K_2HPO_4)
- **Results**
  - Average TCE/TCA removal - > 80%

Conclusions of SBR/FBR Anaerobic Results

- FBR provided 80% reduction at 4-hour HRT vs 70% reduction at 13-hour HRT with SBR. 4-hour HRT better for full-scale design.
- GAC provided better destruction than plastic for FBR
- Conclusion: FBR for full-scale

Aerobic Reactor Test: FBR

- 2-L constructed of polyethylene FBR
  - FBR seeded with effluent from the anaerobic FBR
  - Filled with ½" plastic media colonized with site 9 groundwater to 50% fill volume
  - Oxygen introduced through bottom of FBR
- Operating conditions
  - Nutrients (450 mg/L NH_4Cl and 95 mg/L K_2HPO_4)
  - HRT – 4 hours
  - Temperature - 68-77°F (20-25°C)
- Results: COD loading was reduced by approximately 70%

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Summary of Bench Results and Conclusions

- Bench-scale results
  - Anaerobic FBR reduced TCE/TCA > 80% at a 4-hour HRT
  - Aerobic FBR reduced COD approximately 70%
- Biological processes were shown to be effective in treating site groundwater
- The HRT was effectively reduced from 13 hours to 4 hours with the addition of an electron donor achieving equal or better results
- FBR more effective than SBR
- GAC better than plastic in anaerobic
- Proceed with pilot-scale testing

Groundwater Treatment Pilot Test

Pilot Test Objectives

- Objectives
  - Verify bench test results using real time field conditions (influent groundwater, weather conditions, process interruptions, etc.)
  - Verify robustness of anaerobic biological process
  - Size full-scale system (HRT, O_2 system, electron donor, and nutrients)
  - Evaluate sequential operation to optimize mass destruction
    - Anaerobic followed by aerobic

Pilot Test Biological System

Anaerobic FBR

- **Anaerobic FBR**
  - 12” diameter PVC reactor
  - Filled to a settled bed height of 74” with GAC pre-wetted with Site 9 groundwater
  - Seeded with primary anaerobic sludge and anaerobic biomass from an existing TCE plume
  - Initially fluidized to 95” (28% fluidization)
- **Operating parameters**
  - Flow rate - 0.15 gpm
  - HRT - 5 hours
  - Electron donor (Sodium Benzoate) - flow rate 6 gpd
  - Nutrient (phosphorous and nitrogen) – 3.6 gpd
  - Temperature 90-97°F (32-36°C)

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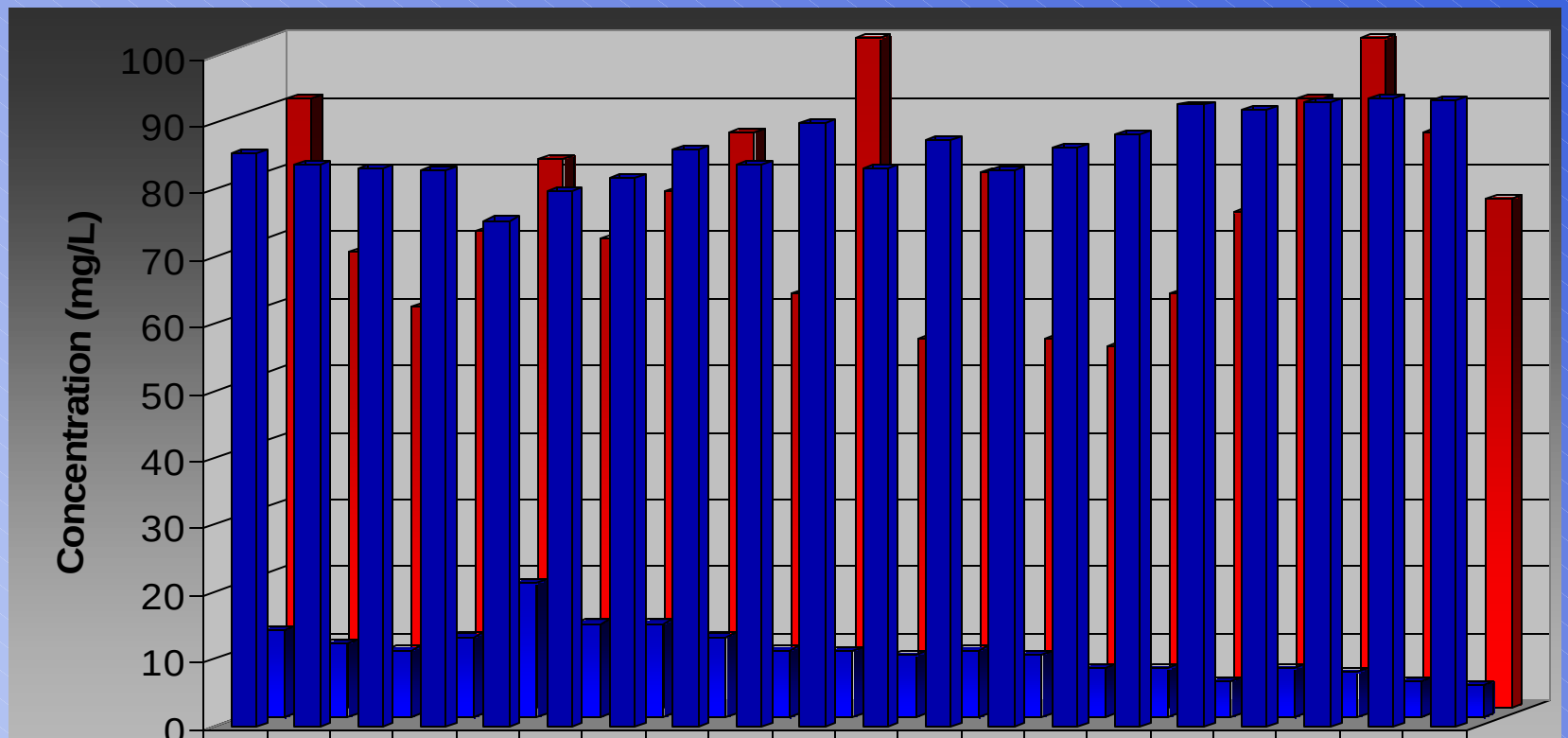
Anaerobic FBR Results

- Average TCE/TCA removal - > 83%
- No increase in cis 1,2-DCE or vinyl chloride

Compound	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Percent Reduction
TCE	85	10	86
cis 1,2-DCE	33	26	20
Vinyl Chloride	0.6	0.7	---
1,1,1-TCA	29	5	83
Methylene Chloride	12	9	23

TCE Removal in the Anaerobic FBR



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TCE Influent	76	86	100	91	74	62	54	55	80	55	100	62	86	77	70	82	71	60	68	91
TCE Effluent	4.9	5.3	6.6	7.2	5.3	7.2	7.3	9.3	10	9.2	9.9	10	12	14	14	20	12	10	11	13
Percent Reduction	94	94	93	92	93	88	86	83	88	83	90	84	86	82	80	76	83	83	84	86

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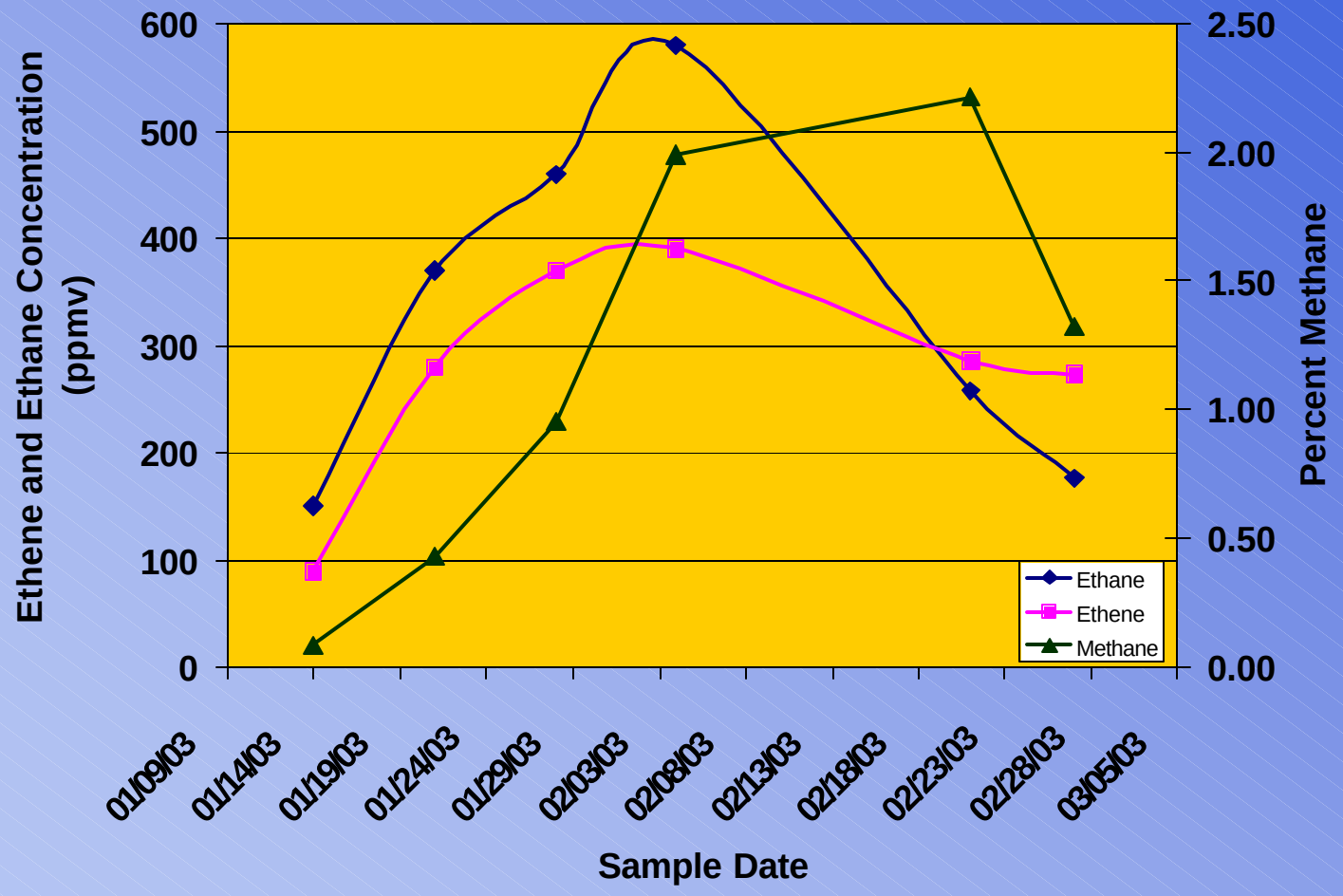
Anaerobic Mechanisms: What's going on?

- Nitrate reduction – NO, very low nitrate in influent groundwater, no reduction measured
- Iron reduction – NOT OBSERVED, data inconclusive
- Sulfate reduction – YES, sulfate concentrations reduced, sulfide increased
- Methanogenesis – YES, methane concentrations increased both in liquid and vapor phase
- Ethene/Ethane concentrations (vapor phase) increased

Ethene, Ethane, and Methane:
Vapor Phase



Anaerobic Mechanisms (cont.)

- **Highlight**
  - **Dehalococcoides Ethenogenes (DHE) present in the anaerobic culture indicating complete dechlorination is actively occurring**
    - **No accumulation of daughter products**
    - **Ethene generation**
- **Vapor/Water Mass Balance**
  - **Total VOCs removed in water phase – 0.1941 lb/day (99.78%)**
  - **Total VOCs removed in vapor phase – 0.0004 lb/day (0.22%)**

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Aerobic FBR

- **Aerobic FBR**
  - 12” diameter stainless steel reactor
  - Filled to a settled bed height of 60” with GAC pre-wetted with Site 9 groundwater
  - Seeded with secondary clarifier sludge
  - Initially fluidized to 76” (28% fluidization)
- **Operating parameters**
  - Flow rate - 0.13 gpm (20% less than influent feed to anaerobic FBR)
  - HRT - 5 hours
  - Electron donor and nutrient supplied by anaerobic biomass carryover
  - Temperature 68-77°F (20-25°C)
  - Dissolved Oxygen – 2.0 ppm

Aerobic FBR Results

- TCE/TCA removal - > 95% average
- Significant reduction in TCE daughter products (cis 1,2-DCE and VC) - > 90% average
- COD reductions - > 85%
- Phenol reductions - > 99%

Compound	Influent Concentration (mg/L)	Effluent Concentration (mg/L)	Percent Reduction
TCE	10	0.3	97
cis 1,2-DCE	26	3	89
Vinyl Chloride	0.7	0.04	94
1,1,1-TCA	5	0.16	97
Methylene Chloride	9	2	72

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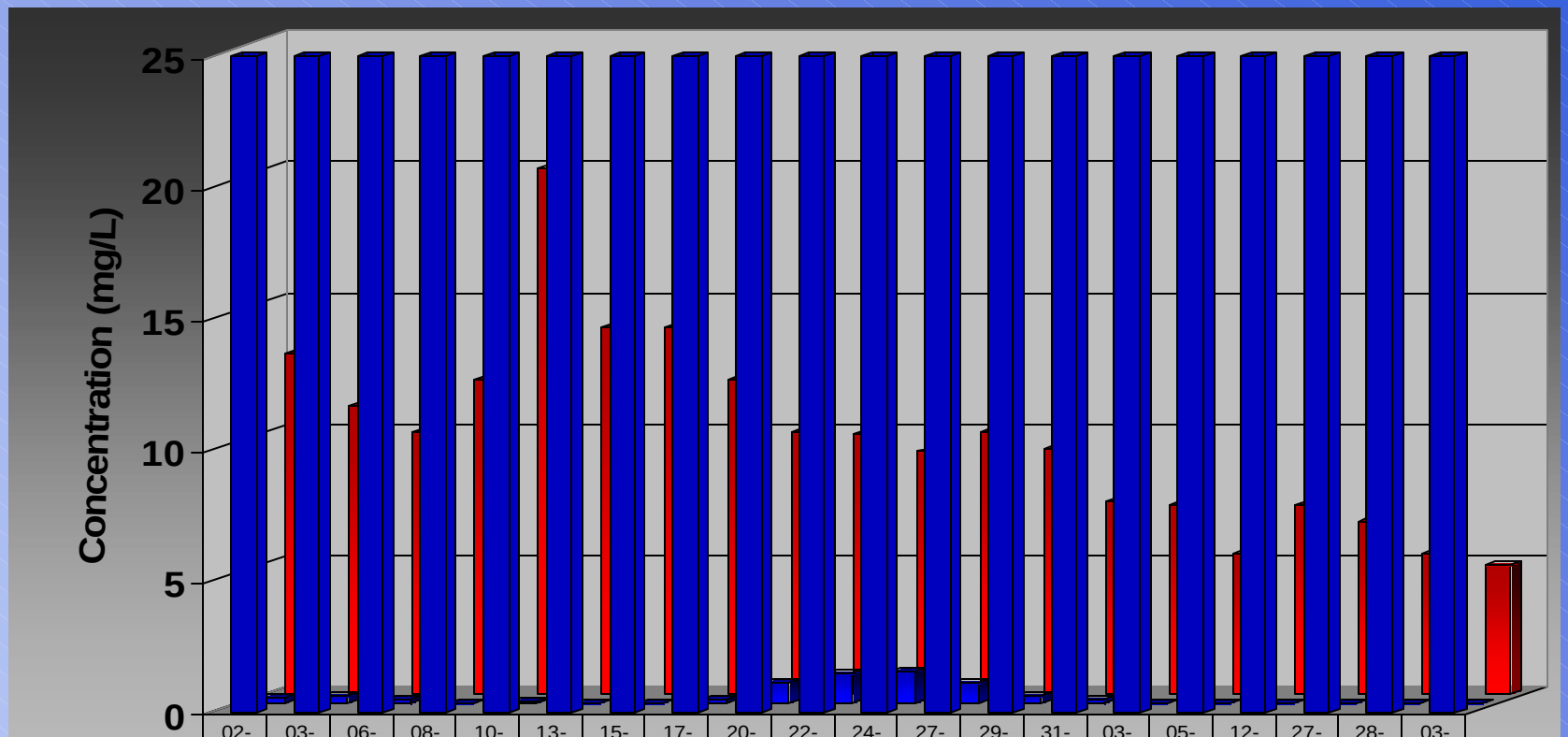
TCE Removal in the Aerobic FBR



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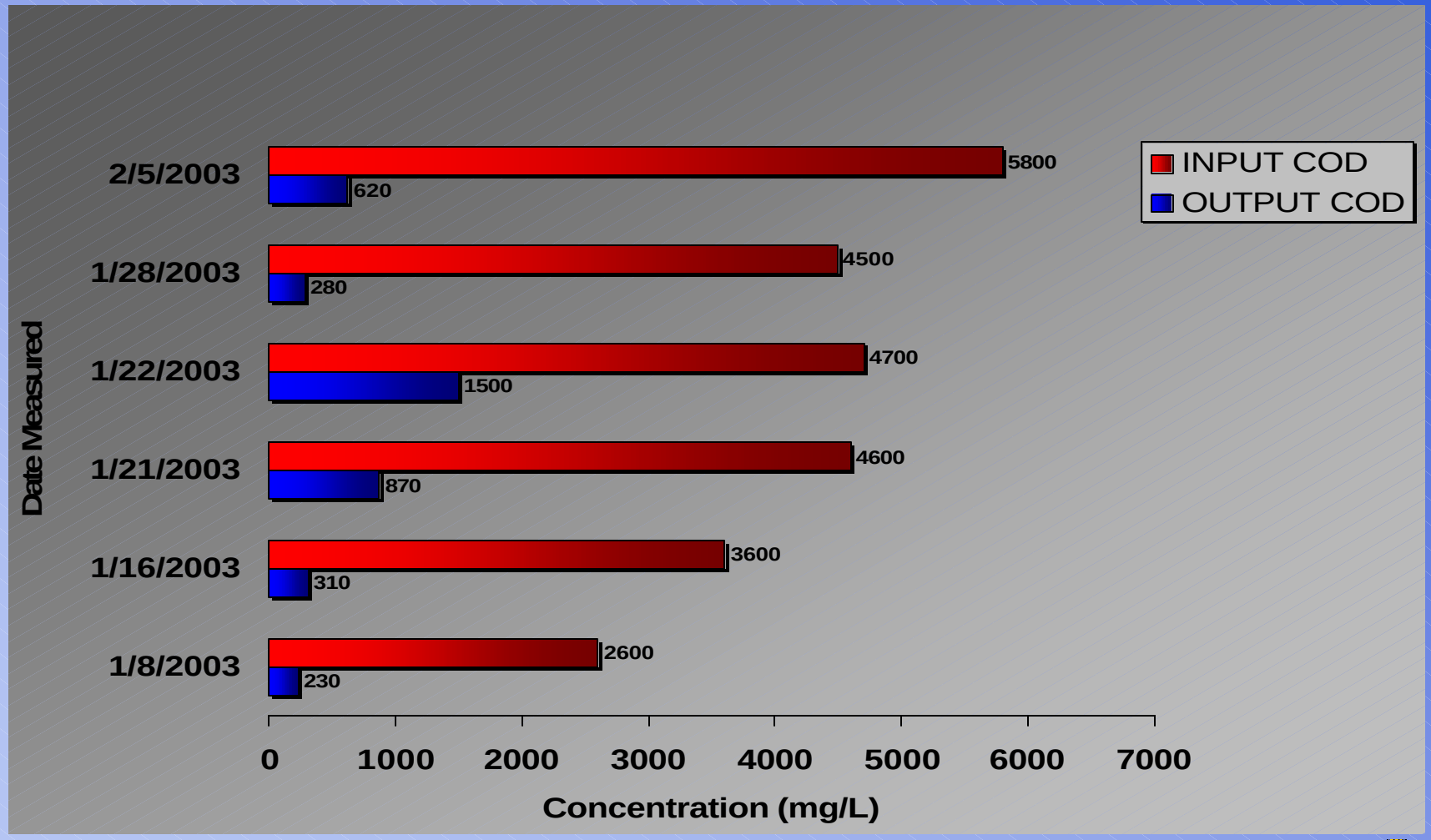
TCE Influent	4.9	5.3	6.6	7.2	5.3	7.2	7.3	9.3	10	9.2	9.9	10	12	14	14	20	12	10	11	13
TCE Effluent	0.0	0.0	0.0	0.0	0.0	0.0	0.11	0.24	0.75	1.2	1.1	0.81	0.16	0.0	0.0	0.1	0	0.15	0.27	0.22
Percent Reduction	100	100	100	100	100	98	98	97	93	87	89	92	99	100	100	100	100	99	98	98

COD Removal in the Aerobic FBR



Aerobic Mechanisms: What's going on?

- **Stripping…..NO!**
  - **Mass balance --- concentrations in the vapor phase accounted for less than 1% of total mass removal**
  - **Measured dissolved oxygen concentrations decreased through reactor**
  - **No visual signs of stripping within reactor (oxygen bubbles)**
- **Cometabolism…..YES!**
  - **Previous work at Moffet Federal Air Field (1990-1998)**
  - **Necessary substrates present**
    - **Methane: demonstrated for reduction of TCE, cDCE, VC**
    - **Ammonia: demonstrated for reduction of TCA and TCE, cDCE, VC**
    - **Phenol: demonstrated for reduction of TCE, cDCE, VC**

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Summary of Results

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- Anaerobic treatment reduced TCE/TCA by approximately 85% at a 5-hour HRT
- Aerobic oxidation and cometabolism reduced COD loading by approximately 85% and TCE/TCA by approximately 90%
- Sequential anaerobic/aerobic treatment was effective in reducing TCE/TCA by approximately 99% and COD loading by approximately 85%

Summary of Results

Compound	Anaerobic Influent (mg/L)	Anaerobic Effluent (mg/L)	Aerobic Effluent (mg/L)	Anaerobic Percent Removal	Aerobic Percent Removal	Total Percent Removal
TCE	85	10	0.3	86	97	97
cis 1,2-DCE	33	26	3	20	89	91
Vinyl Chloride	0.6	0.7	0.04	---	94	93
1,1,1-TCA	29	5	0.2	83	97	99
Methylene Chloride	12	9	2	23	72	83

Conclusions

Conclusions

- Fluidized-Bed Sequential Biological Treatment is effective in treating site groundwater
- 5-hr HRT will provide > 90% destruction of site compounds
- Anaerobic process shown to be very robust
  - Changing field conditions (influent groundwater)
  - Temperature changes
  - Process interruptions

Next Steps

- Determine most effective electron donor
- Reduce HRT – can sufficient destruction be achieved?
  - Initial results promising
    - Anaerobic TCE removal 57% average at a 2.5-hour HRT
    - Aerobic TCE removal 93% average at a 2.5-hour HRT

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